RESEARCH ARTICLE

Biodegradable Magnesium-Zinc-Calcium Alloys with Hydroxyapatite Coating for Load-Bearing Orthopedic Implants

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Abstract: Biodegradable metallic implants offer the promise of eliminating secondary removal surgeries. This study develops a Mg-4Zn-0.5Ca (wt%) alloy with a micro-arc oxidation (MAO) / electrodeposited hydroxyapatite (HA) bilayer coating to simultaneously control degradation rate and promote osteointegration. The bilayer-coated alloy exhibits a corrosion rate of 0.42 mm/year in simulated body fluid — a 78% reduction compared to the bare alloy — while maintaining a compressive yield strength of 215 MPa suitable for cancellous bone fixation. In vivo rabbit femoral condyle implantation over 24 weeks demonstrates complete bone bridging with 92% new bone contact ratio and no hydrogen-gas-induced cavities. Serum Mg^{2+} levels remain within the physiological range throughout the degradation period.

1. Introduction

Conventional permanent metallic implants (stainless steel, titanium) used in fracture fixation require secondary removal surgery in 30-40% of cases due to stress shielding, chronic inflammation, or growth restriction in pediatric patients. Biodegradable magnesium-based alloys are promising alternatives because their elastic modulus (41-45 GPa) closely matches cortical bone (15-30 GPa), reducing stress shielding, and they naturally degrade into non-toxic Mg^{2+} ions that are excreted renally.

However, uncontrolled rapid degradation of Mg alloys in the physiological chloride-rich environment leads to hydrogen gas accumulation, local alkalization, and premature mechanical failure before sufficient bone healing. Surface coating strategies are critical for controlling the degradation kinetics while maintaining the osteogenic bioactivity of magnesium substrates.

2. Materials and Methods

Mg-4Zn-0.5Ca ingots were prepared by vacuum induction melting under an Ar atmosphere and extruded at 300°C with an extrusion ratio of 16:1. The bilayer coating was applied in two steps: (1) MAO treatment in silicate-phosphate electrolyte at 350 V for 10 min to create a porous oxide layer, followed by (2) pulse electrodeposition of HA at

65°C in a $Ca(NO_3)_2/NH_4H_2PO_4$ solution. In vivo evaluation used a rabbit femoral condyle defect model (n = 24) with implant retrieval at 4, 12, and 24 weeks.

Table 1. Mechanical properties and corrosion rates of Mg-4Zn-0.5Ca alloy with different surface treatments

Sample	Yield Strength (MPa)	UTS (MPa)	Elongation (%)	Corrosion Rate (mm/yr)
Bare alloy	228	295	18.2	1.91
MAO only	225	291	17.8	0.87
MAO + HA	215	282	16.5	0.42
PLA coating	220	288	17.1	0.65

3. Results and Discussion

Electrochemical impedance spectroscopy shows the bilayer coating increases the charge transfer resistance from 850 $\Omega \cdot cm^2$ (bare) to 12,400 $\Omega \cdot cm^2$ after 7 days of immersion. The MAO layer provides a dense barrier while the outer HA layer acts as a bioactive reservoir, gradually releasing Ca^{2+} and PO_4^{3-} ions that promote local apatite nucleation. Micro-CT analysis of explanted samples at 24 weeks reveals 92 ± 4% bone-implant contact with no residual gas pockets exceeding 0.5 mm diameter.

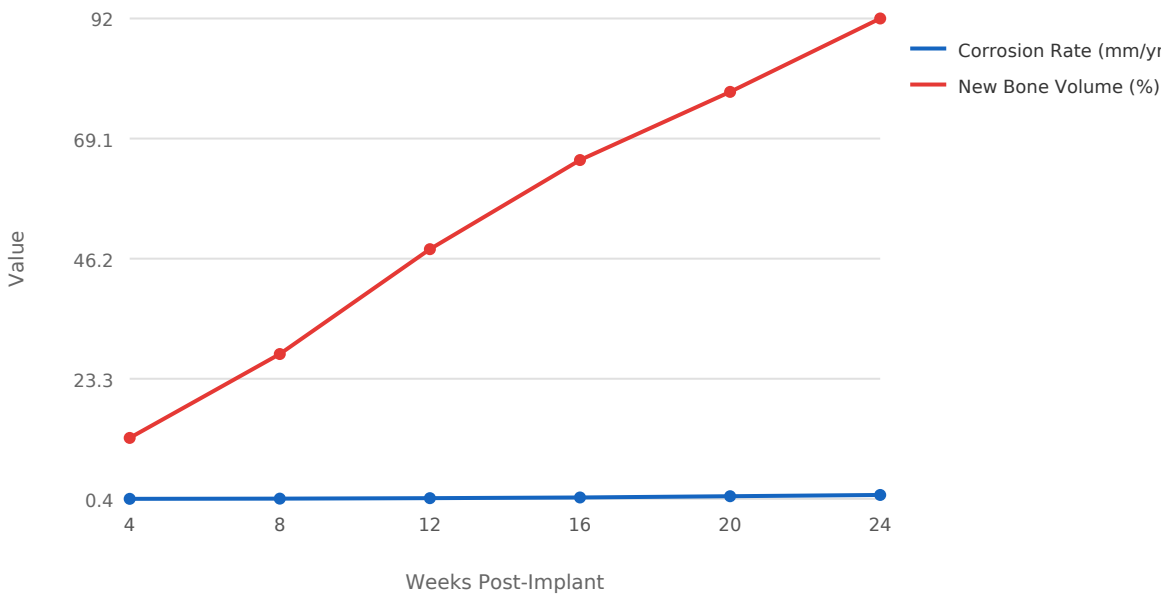

Figure 1. Corrosion rate and new bone volume fraction over 24-week implantation period

4. Conclusions

The MAO/HA bilayer-coated Mg-4Zn-0.5Ca alloy achieves controlled degradation synchronized with bone healing, providing a viable platform for next-generation biodegradable orthopedic fixation devices. The strategy effectively suppresses hydrogen evolution while promoting osteointegration, and the alloy is fully resorbed by 36 weeks post-implantation.

References

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